Synthesis and Characterization of the Novel Al^I Compound $Al(C_5Me_4Ph)$: Comparison of the Coordination Chemistry of $Al(C_5Me_5)$ and $Al(C_5Me_4Ph)$ at d^{10} Metal Centers[1)]

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Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. The synthesis of the novel Al^I compound $AlCp^{*Ph}$ ($Cp^{*Ph} = C_5Me_4Ph$) is presented. This compound is characterized by ^1H, ^{13}C, ^{27}Al NMR spectroscopy, elemental analysis as well as its reactivity towards the α,ω-diolefin dvds (dvds = tetramethyl-divinyl-disiloxane). Also the reactivity of $AlCp^*$ towards dvds is investigated and the product $[(dvds)(\mu_2\text{-}AlCp^*)_2]$ characterized by NMR spectroscopy, elemental analysis as well as X-ray crystallography. Furthermore, two new coordination compounds of $AlCp^*$ to d^{10} metal centers are synthesized and characterized. $[Pd(AlCp^*)_4]$ is obtained by reaction of $[(tmeda)PdCl_2]$ with $AlCp^*$, and $[Ni(AlCp^*)_4]$ is synthesized from $[Ni(cod)_2]$ and $AlCp^*$ *via* ligand substitution. Both complexes are spectroscopically and crystallographically characterized. Finally, preliminary results on the coordination of $AlCp^{*Ph}$ to Ni^0 and Pd^0 centers will be discussed.

Keywords: Aluminum; Carbenoid ligands; Palladium; Nickel; Coordination chemistry

Introduction

Low valent, carbenoid aluminum compounds of the general type $[AlR]_n$ have attracted considerable interest not only because of fundamental issues in terms of structure and bonding but even more attention is due their unique reactivity including ligand properties in coordination chemistry. With increasing atomic number within the group 13, the stability of E^I compounds increases and correspondingly their chemical reactivity decreases. Thus, amongst all low valent group 13 species, Al^I compounds are unique. In particular, they are significantly more reactive than Ga^I, In^I or Tl^I compounds, what is also reflected by their rich coordination to transition metals. In general, Al^I compounds are very potent σ-donors and strongly increase the electron density of transition metal centers on coordination, while the Al atoms become very electrophilic. In contrast to the potentially even more reactive organo B^I compounds, if they were accessible as monomers, the organo Al^I congeners are stable and isolable and can be used as novel starting compounds for synthesis. This, of course, especially allows their use as ligands in coordination chemistry. However, their preparation is neither simple nor straightforward, what made them chemically inaccessible until as late as the 1990's. The first synthesis of $AlCp^*$ was reported by *Schnöckel*, who treated a metastable solution of AlCl with $MgCp^*_2$ [1]. The major problem in this route is the preparation of the high temperature species AlCl, which has to be done by high temperature gas phase reaction of Al and HCl and rapid condensation of the product in an excess of a solvent mixture (e.g. toluene/THF). This is a rather sophisticated and not generally available technique. The credit of having provided the inorganic chemist′s community with a more easily applicable laboratory protocol for the synthesis of $AlCp^*$ goes to *Roesky* et al. who obtained $AlCp^*$ *via* reductive dehalogenation of Cl_2AlCp^* with potassium in 1993 [2]. The rather low yield of this reaction could subsequently be considerably increased by simply using Br_2AlCp^* instead of the chloride derivative and using Na/K alloy as the reducing agent [3a]. Thus, $AlCp^*$ can now be prepared in reproducible overall yields of 40-50 %, starting from $AlBr_3$ and Cp^*SiMe_3. We entered this scene in 1997 when we published the synthesis of $[(CO)_4FeAlCp^*]$ from $K_2[Fe(CO)_4]$ and Cl_2AlCp^* which at that time was the first example of a $AlCp^*$ ligand in a terminal coordination mode at a transition metal fragment [16]. Since then a number of groups were active to study the ligand properties of low valent group-13 species. Our major research interest in the field has been to obtain homoleptic, *i.e.* CO-free, metal rich cluster compounds of the general type $[M_a(ER)_b]$ and elucidate their chemistry including the potential of that chemistry for advanced materials, *e.g.* nanoclusters of intermetallic compounds M_xE_y [4]. We have reported on novel clusters of the types $M_2(ECp^*)_5$ or $M_3(ECp^*)_n$ (M = Pd, Pt; n = 6, 8), their structures being without direct precedence in classical CO or phosphine cluster chemistry [5−8]. In contrast to the related Ga and In chemistry, the coordination of $AlCp^*$ to a transition metal centers causes the Al centre to become

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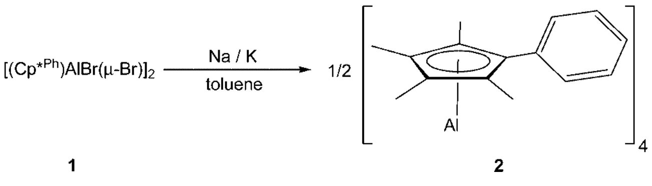
very electrophilic and prone to subsequent reactions. Thus, the reaction of $[Ni(cod)_2]$ with AlCp* in benzene does neither lead to homoleptic monomeric $[Ni(AlCp^*)_4]$ nor cluster structures $[Ni_a(AlCp^*)_b]$, but instead yields a new complex of the formula $[Ni(AlCp^*)_3\{AlCp^*(Ph)\}(H)]$ by C-H activation of the solvent [9]. The product was shown to be formed *via* the reactive intermediate $[Ni(AlCp^*)_3]$. Similarly, the Fe^0 source $[Fe(\eta^6\text{-toluene})(\eta^4\text{-1,3-butadiene})]$ reacts with AlCp* under full ligand substitution giving unusual C-H activated isomers of $[Fe(AlCp^*)_5]$. [10] In order to stabilize reactive intermediates $[M(ER^*)_n]$ and to study their chemistry in more detail, increasing the steric bulk of the Cp*-type ligand appears to be a strategy. Maybe, that the formation of the kinetically inert, inreactive monomer $[Ni(AlCp^*)_4]$ can be suppressed, which compound represents the thermodynamic sink in all substitution reactions we have studied so far. In this paper we wish to report on the synthesis and characterization of the new, bulky ligand $AlCp^{*Ph}$ as well as the reactions of AlCp* and $AlCp^{*Ph}$ with the di-olefin dvds (dvds = tetramethyl-divinyl-disiloxane). In addition, the coordination chemistry of AlCp* and $AlCp^{*Ph}$ to Ni^0 and Pd^0 will be compared looking into their reactions with $[(tmeda)PdCl_2]$ and $[Ni(cod)_2]$.

Results and Discussion

Synthesis and Characterization of $AlCp^{*Ph}$ (2)

The preparation of $AlCp^{*Ph}$ (**2**) is carried out analogously to the procedure published for AlCp*. Compound **2** is synthesized from $[Cp^{*Ph}AlBr(\mu\text{-}Br)]_2$ (**1**), which is obtained from $Cp^{*Ph}SiMe_3$ and $AlBr_3$ in hexane. Reduction of **2** with a Na/K alloy in toluene gives a yellow solution and a light gray precipitate. After filtration and removal of the solvent *in vacuo*, the oily residue is recrystallized from diethylether giving pure **2** as a yellow powder in reproducible yields of 70 % (Scheme 1). The main differences of this procedure to the classical preparation described in literature for AlCp* arises from the good solubility of **2** in toluene in contrast to AlCp*. Compound **2** is also very well soluble in warm *n*-hexane. Thus, all attemps to crystallize **2** failed, so far. No definite conclusions concerning the structure of **2** in solid state or in solution, *i.e.* the degree of association, can be made at this point, but a tetrameric structure $[AlCp^{*Ph}]_4$ analogously to $[AlCp^*]_4$ is assumed.

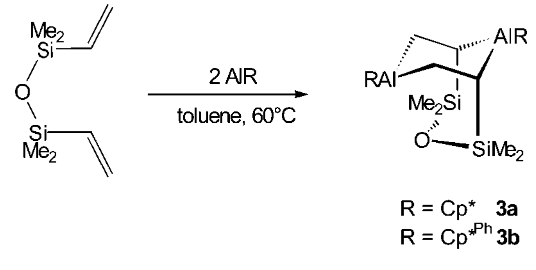


Scheme 1 Preparation of **2**

However, the chemical nature of the obtained product **2** was confirmed by NMR spectroscopy, elemental analysis as well as its chemical reactivity towards the α,ω-diolefin dvds. The ^1H NMR spectrum of **2** in C_6D_6 exhibits two singlets at 1.92 and 1.77 ppm for the methyl groups and a multiplet at 7.46-7.15 ppm for the phenyl group. The ^{13}C NMR shows four signals for the phenyl group (δ = 136.8/131.0/ 130.3/126.1) and two sets of signals for the Cp* methyl groups (δ = 121.8/116.1/ 115.1 and 12.1/11.1). The ^{27}Al NMR spectrum exhibits one signal at −102.5 ppm. This signal is remarkably downfield-shifted with respect to the ^{27}Al NMR signal of $[AlCp^*]_4$ (−81 ppm), but still significantly lower than the signals for the monomers $Al[C_5(CH_2Ph)_5]$ and $Al[C_5H_2(SiMe_3)_3]$ (−155 and −165 ppm, respectively). [1b] Thus, also the ^{27}Al-NMR does not lead to definite conclusions concerning the degree of association of **2** in solution, but the existence of aggregates other than $[AlCp^{*Ph}]_4$ cannot be excluded on this basis.

Reaction of AlCp and $AlCp^{*Ph}$ with dvds*

Recently we reported on the synthesis of the novel trinuclear compound $[Pd_3(AlCp^*)_2(\mu_2\text{-}AlCp^*)_2(\mu_3\text{-}AlCp^*)_2]$, which was obtained by reaction of $[Pd_2(dvds)_3]$ with an excess of AlCp* in benzene at 60 °C [8]. The formation of monomeric $[Pd(AlCp^*)_4]$ or dimeric $[Pd_2(AlCp^*)_5]$ was not observed. During this reaction the colorless product $[(dvds)(\mu_2\text{-}AlCp^*)_2]$ (**3a**) is formed as a by-product, thus excess AlCp* is consumed by dvds. The independent treatment of free dvds with two equivalents of AlCp* in toluene at 60 °C in absence of Pd^0 complexes affords a colorless solution. Crystallization at −30 °C affords **3a** as colorless crystals in a yield of 83 %. Analogously, reaction of dvds with two equivalents of $AlCp^{*Ph}$ in toluene leads to the adduct $[(dvds)(\mu_2\text{-}AlCp^{*Ph})_2]$ (**3b**) in a yield of 60 %. Both complexes are air sensitive and readily dissolve in non polar organic solvents such as benzene or toluene (Scheme 2).



Scheme 2 Synthesis of $[(dvds)(\mu_2\text{-}AlR)_2]$ (R = Cp* **3a**, Cp^{*Ph} **3b**)

The ^1H NMR spectrum of **3a** in C_6D_6 exhibits two singlets at 1.96 and 1.95 ppm for the methyl groups of the two AlCp* ligands. The dvds group shows four signals, which can be assigned as follows: The four protons of the two CH_2 groups give rise to one broad multiplet due to geminal and vicinal coupling in the range of 0.55-0.32 ppm. A broad triplet at −0.26 ppm (*J*(H,H) = 8.7 Hz) represents the CH moieties, and the two singlets at 0.29 and 0.11 ppm can be assigned to the $SiMe_2$ groups. The ^{13}C NMR spectrum reveals two sets of signals for the Cp* groups (δ = 114.3/114.1 and 10.7/10.6). The CH und CH_2 groups give

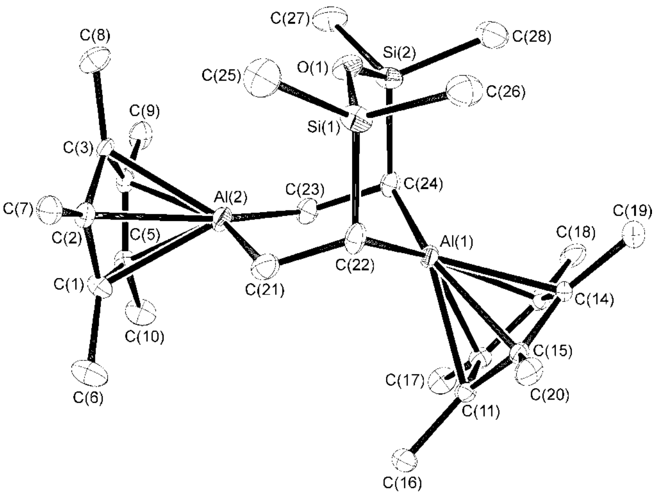


Figure 1 Molecular structure of [(dvds)(μ_2-AlCp*)$_2$] (**3a**) (thermal ellipsoids set at 30 % probability). Selected bond lengths /Å and angles /°:
Al(1)-C(22) 2.002(4), Al(1)-C(24) 1.991(4), Al(2)-C(21) 1.968(4), Al(2)-C(23) 1.993(4), Si(1)-O(1) 1.656(3), Si(1)-C(22) 1.908(4), Si(1)-C(25) 1.868(5), C(21)-C(22) 1.551(6), Cp*$_{centroid}$-Al(1) 1.947, Cp*$_{centroid}$-Al(2) 1.952, C(22)-Al(1)-C(24) 106.24(17), C(21)-Al(2)-C(23) 108.64(18), Al(1)-C(22)-C(21) 109.0(3), Al(2)-C(21)-C(22) 118.0(3), Al(1)-C(22)-Si(1) 109.5(2), C(22)-Si(1)-O(1) 109.26(17), Si(1)-O(1)-Si(2) 134.50(17), C(25)-Si(1)-C(26) 108.6(2), Al(1)-C(22)-C(21)-Al(2) 54.6(4), Al(1)-C(22)-Si(1)-O(1) 45.6(2).

rise to two broad resonances at 13.8 and 10.1 ppm, respectively. The two signals at 3.6 und −0.2 ppm can be assigned to the SiMe$_2$ moieties. Interestingly, no ^{27}Al signal is visible. Presumably, the two Al^{III} resonances are covered by the broad peak of the probe head (δ = 66.8).

The NMR spectra of **3b** are very similar to **3a**. The ^{1}H NMR spectrum of **3b** in C$_6$D$_6$ exhibits four singlets at 2.08, 2.03, 2.00 and 1.99 ppm for the Cp*^{Ph} methyl groups and a multiplet at 7.11-7.49 ppm for the phenyl group. For the dvds part four signals are found: a broad multiplet at 0.59 ppm for the CH$_2$ groups, two singlets at 0.25 and 0.13 ppm for the SiMe$_2$ groups and a triplet at −0.13 ppm for the CH groups. Also in the ^{13}C NMR spectrum, two sets of signals for the AlCp*^{Ph} ligands are found, indicating their slightly different chemical environment. Thus there are eight signals for the phenyl groups (δ = 136.2, 135.9, 131.0, 130.8, 128.9, 128.8, 128.5 and 126.5). The Cp* parts give rise to overall nine signals (δ = 121.6, 120.3, 117.5, 117.3, 114.7, 114.6 for the ring carbon atoms and 12.1 (2 C), 11.0, 10.9 ppm for the methyl groups). Two broad signals at 14.0 and 10.8 ppm can be assigned to CH and CH$_2$ groups, respectively. The SiMe$_2$ groups result in two signals (δ = 3.9 and −0.1). As in the spectrum of **3a** there is no ^{27}Al signal visible.

Suitable crystals of **3a** can be obtained by stepwise cooling a concentrated solution in toluene to a final temperature of −30 °C. Important crystallographic data are summarized in Table 1. The molecular structure of **3a** is depicted in Figure 1.

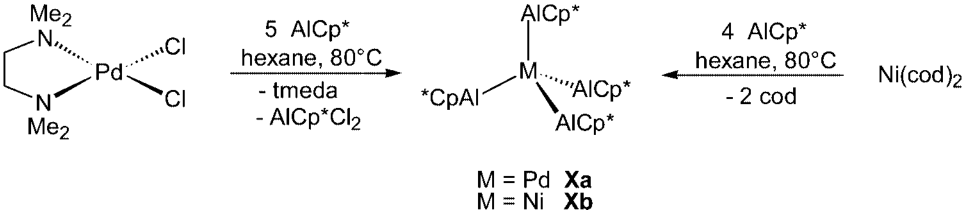
Compound **3a** crystallizes in the orthorhombic space group *Pbca*. The molecular structure represents an adduct of two AlCp* units to the two C=C double bonds of one dvds ligand, resulting in a ninemembered bicyclic ring comparable to 9-BBN. Analogous olefin adducts of Al^I were recently synthesized and characterized in the literature [11, 12]. The central C, Si and Al atoms of the bicyclus show only a small distortion, which is documented by the respective coordination sphere of these atoms. Thus, the angles C-Al-C, Al-C-C, Al-C-Si and C-Si-C with values in the range of 106.24(17)° (C(22)-Al(1)-C(24)) and 118.0(3)° Al(2)-C(21)-C(22) only slightly deviate from an ideal tetrahedral environment. As expected, the angle Si(1)-O(1)-Si(2) (134.50(17)°) is significantly widened. The distances Al(1)-C(22,24) and Al(2)-C(21,23) are found in the range of 1.991(4)-2.002(4) Å, corresponding to the bond lengths in the Cp*Al^{III} compounds [{Cp*AlRCl}$_2$] (R = Me 1.931 Å [13], R = ^{i}Pr 1.951 Å [14]). The Cp*$_{centroid}$-Al distances in **3a** (Cp*$_{centroid}$-Al(1) 1.947, Cp*$_{centroid}$-Al(2) 1.952) are similar to those in [{Cp*AlRCl}$_2$] (1.952 and 1.947 Å), while the Cp*$_{centroid}$-Al distances in [{Cp*AlCl$_2$}$_2$] (1.871 Å) or in the mono substituted metal carbonyls [(CO)$_5$Cr-AlCp*] (1.819 Å) [15] and [(CO)$_4$Fe-AlCp*] (1.775 Å) [16] are significantly shortened. The bonds C(21)-C(22) (1.551(6) Å) and C(23)-C(24) (1.568(6) Å) can be unequivocally identified as C-C-single bonds. In contrast, in the complex [(dmi)Pd(dvds)] (dmi = 1,3-dimesitylimidazoline-2-ylidene) the ligand dvds is π-coordinated, giving C-C distances of 1.408(6) Å and 1.388(6) Å [17].

Synthesis of M(AlCp)$_4$ (M = Ni, Pd) and Comparison of the Coordination Chemistry of AlCp* and AlCp*^{Ph} to Pd^0 and Ni^0*

While numerous M-E compounds with E = Ga or In have been synthesized in the past decade, only a small number of examples of transition metal complexes bearing AlCp* as a ligand are known [9, 16, 18]. In particular, the existing class of homoleptic clusters [M$_a$(E^{I}R)$_b$] (M = Ni, Pd, Pt; E = Al, Ga, In; R = Cp*, C(SiMe$_3$)$_3$) is still focused on gallium and indium containing ligands. As described above, the reaction of [Pd$_2$(dvds)$_3$] with an excess of AlCp* leads to the trimetallic compound [Pd$_3$(AlCp*)$_6$]. Also the dinuclear compound [Pd$_2$(AlCp*)$_5$] is accessible, but only "indirectly" *via* ligand substitution of GaCp* *versus* AlCp* in [Pd$_2$(GaCp*)$_5$] [8]. However, in these ligand substitution reactions the formation of the monomeric, saturated compound [Pd(AlCp*)$_4$] was never observed.

Analogously to the synthesis of [Pd(GaCp*)$_4$] and [Pd{InC(SiMe$_3$)$_3$}$_4$] [6], treatment of [(tmeda)PdCl$_2$] with exactly five equivalents of AlCp* in hexane at 80 °C for 3 h results in the formation of the monomeric complex [Pd(AlCp*)$_4$] (**4a**) via reductive coordination of AlCp* with Cl$_2$AlCp* being the by-product (Scheme 3). Crystallization from hexane at −30 °C gives **4a** as air-sensitive yellow crystals in a good yield of 81 %.

As already described in a previous publication, the reaction of [Ni(cod)$_2$] with four equivalents of AlCp* in hexane at 80 °C leads to a full substitution of the cod ligands, giv-



Scheme 3 Synthesis of $[M(AlCp^*)_4]$ (M = Pd **4a,** M = Ni **4b**)

ing the monomeric Ni^0 complex $[Ni(AlCp^*)_4]$ (**4b**) as yellow crystals in a yield of 90 % [9]. However, this complex was not fully discussed in the original communication, and is therefore included herein and characterized in more detail.

Both complexes dissolve well in non polar organic solvents such as hexane or toluene and decompose at 123 °C (**4a**) and 94 °C (**4b**). The NMR spectra of **4a** and **4b** are rather simple, as expected for highly symmetric homoleptic compounds with η^5-coordinated Cp* rings. The ^{1}H-NMR spectrum of **4a** in C_6D_6 shows one singlet at 1.92 ppm (**4b**: $\delta = 1.92$) and the ^{13}C-NMR shows two resonances at 113.0 (C_5Me$_5$) and 10.8 (C$_5$$Me_5$) ppm (**4b**: $\delta = 112.9/10.7$), respectively. The ^{27}Al-NMR of **4a** in C_6D_6 shows one broad resonance at -67.2 ppm, which is shifted to higher field compared to **4b** ($\delta = -37.3$).

Analogously to the reaction of $[(tmeda)PdMe_2]$ with GaCp* or $InC(SiMe_3)_3$ [6], the reduction of Pd^{II} to Pd^0 is accompanied by a transfer of the chlorine atoms to AlCp*, giving the Al^{III} side product $[Cl_2AlCp^*]$, which could be characterized by means of ^{1}H ($\delta = 1.86$) and ^{13}C NMR ($\delta = 116.1/11.0$) spectroscopy. The reaction of $[(tmeda)PdMe_2]$ with AlCp* affords several still unidentified products with only a small content of **4a**, showing that methyl transfer from Pd is less selective for Al in comparison with Ga or In [6]. However, treatment of $[(tmeda)PdCl_2]$ with GaCp* or InCp* leads to $[Cl_2ECp^*]$ (E = Ga, In), but these reactions are again less selective with respect to the formation of $[M(ECp^*)_4]$ and the yields are considerable lower [6, 7]. Preliminary investigations on the coordination chemistry of $AlCp^{*Ph}$ show that it represents a very reactive ligand which is thus quite difficult to handle.

In many examples we could show, that the formation of cluster complexes $[M_a(ECp^*)_b]$ is very sensitive to the reaction conditions and often a mixture of inseparable products is obtained. Only small “windows” of optimal reaction conditions allow the isolation of defined clusters such as $[Pd_3(GaCp^*)_8]$ or $[Pd_3(AlCp^*)_6]$. This is obviously also the case for the more bulky $AlCp^{*Ph}$. Reaction of $[(tmeda)PdCl_2]$ with $AlCp^{*Ph}$ in C_6D_6 results in a dark red solution. The ^{1}H NMR spectrum of this reaction mixture indicates free tmeda as well as several Pd-Al containing species, which could neither be separated nor identified. These observations accentuate once more the delicate complexity of the insertion reactions of E^IR into M-X bonds, which we have more extensively studied for the transition metals Rh and Ru [19, 20]. Similar, the reaction of $[Ni(cod)_2]$ with $AlCp^{*Ph}$ in either hexane or C_6H_6 leads to unidentifiable mixtures of products. However, the fact that no monomers of the type $[M(AlCp^{*Ph})_4]$ were isolated in the two cases studied indicates well, that the formation of clusters with a ratio of Al:M < 4 is favored over that of monomers just by the small change of one methyl to phenyl in the Cp* ring of AlCp*.It should be pointed out, that this change also increases the solubility of $[AlCp^{*Ph}]_4$ very much over the parent $[AlCp^*]_4$ which is likely to have a significant impact on the kinetics of the reactions. The higher solubility is certainly a major advantage of $AlCp^{*Ph}$ with respect to the unsubstituted AlCp*, as reactions can be carried out at considerably lower temperatures and may be more easily followed by in situ NMR studies.

Structural Properties of 4a and 4b

Suitable crystals of **4a** and **4b** could be obtained by stepwise cooling a concentrated solution in hexane to a final temperature of -30 °C. Important crystallographic data are summarized in Table 1. The molecular structures of **4a** and **4b** are depicted in Figure 2 (as the structural differences of **4a** and **4b** are very small, both compounds are displayed in one Figure). Both complexes crystallize in the tetragonal space group $I\bar{4}$ ($Z = 2$) and are isostructural to all known monomeric complexes of the type $[M(ECp^*)_4]$ [6, 9, 21]. The transition metal atom is tetrahedrally surrounded by four Al atoms with a Al-M-Al angle of 109.26(3)° (**4a**) and 109.43(2)° (**4b**) and a M-Al distance of 2.2950(9) Å (**4a**) and 2.1727(8) Å (**4b**). The Cp* units are nearly symmetrically bonded to the Al atoms with a Al-$Cp^*_{centroid}$ distance of 1.929 Å (**4a**) and 1.933 Å (**4b**), being close to the free ligand of 2.015 Å (gasphase, monomer) [22].

A small deviation from linearity is observed for the $Cp^*_{centroid}$-Al(1)-Pd(1) angles (169.2°). This value is similar to the arrangement in **4b** (173.5°), while homoleptic GaCp* substituted complexes such as $[Pt(GaCp^*)_4]$ (160.7°) [6], $[Pd(GaCp^*)_4]$ (155.5°) [6] and $[Ni(GaCp^*)_4]$ (164.7°) [21] show a significant larger distortion from linearity.

Conclusions

In this paper we presented the isolation and characterization of the new Al^I compound $AlCp^{*Ph}$. The reaction of AlCp* with the diolefin dvds leads to an adduct of two AlCp* units to the two C=C double bonds of one dvds ligand, resulting in a ninemembered bicyclic ring system.

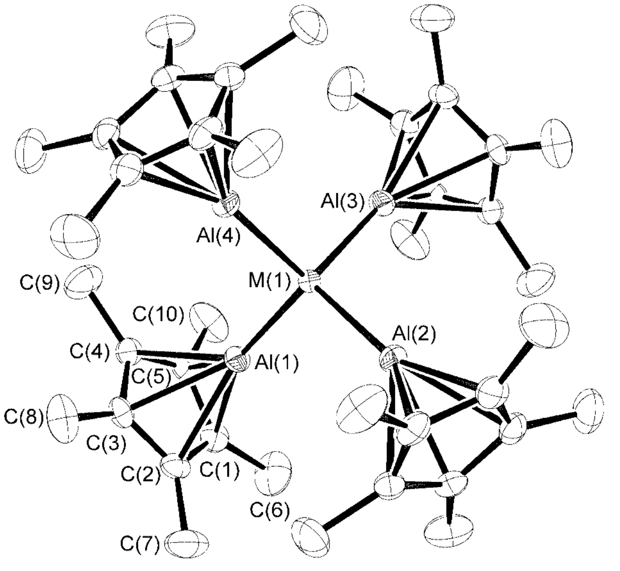


Figure 2 Molecular structure of $[M(AlCp^*)_4]$ (M = Pd **4a**, M = Ni **4b**) (thermal ellipsoids set at 30 % probability). Selected bond lengths /Å and angles /° for

4a: Pd(1)-Al(1) 2.2950(9), Al(1)-C(1) 2.284(3), Al(1)-C(2) 2.284(3), Al(1)-C(3) 2.267(3), Al(1)-C(4) 2.256(3), Al(1)-C(5) 2.265(3), $Cp^*_{centroid}$-Al(1) 1.929, Al(1)-Pd(1)-Al(2) 109.26(3), $Cp^*_{centroid}$-Al(1)-Pd(1) 169.2.
4b: Ni(1)-Al(1) 2.1727(8), Al(1)-C(1) 2.286(3), Al(1)-C(2) 2.285(3), Al(1)-C(3) 2.273(3), Al(1)-C(4) 2.270(3), Al(1)-C(5) 2.273(3), $Cp^*_{centroid}$-Al(1) 1.933, Al(1)-Ni(1)-Al(2) 109.43(2), $Cp^*_{centroid}$-Al(1)-Ni(1) 173.5.

The same product is obtained by reaction of $AlCp^{*Ph}$ with dvds, as indicated by ^1H and ^{13}C NMR spectroscopy, confirming the chemical nature of **2**.

In contrast to AlCp*, the reaction of $AlCp^{*Ph}$ with $[(tmeda)PdCl_2]$ as well as $[Ni(cod)_2]$ did not lead to monomers of the type $[M(AlCp^*)_4]$. The steric bulk which is the result of the substitution of one methyl group in AlCp* to one phenyl group does not allow the coordination of four ligand units to one metal center, thus suppressing the formation of monomers and leading to the formation of clusters. However, the general sensitivity of cluster formation did not allow the isolation of defined cluster complexes. Investigations on the reaction of $AlCp^{*Ph}$ towards more reactive M^0 sources such as [Ni(cdt)] (cdt = t,t,t-cyclododecatriene) or $[Ni(C_2H_4)_3]$, which are expected to allow very mild reaction conditions, are subject of current research. It should be pointed out finally, that the corresponding reactions of $GaCp^{*Ph}$ with the above mentioned Ni^0 and Pd^0 sources have been studied also and a number of well defined products, including for example $[Pd_2(GaCp^{*Ph})_5]$ have been obtaind on which subject we will report elsewhere.

Experimental Section

All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glove box techniques. Hexane, toluene, THF and Et_2O were dried using an mBraun Solvent Purification System, all other solvents were dried by distillation over standard drying agents. The final H_2O content in all solvents used was checked by Karl-Fischer-Titration and did not exceed 5 ppm. $[Ni(cod)_2]$ [23], $[(tmeda)PdCl_2]$ [24], Cp*H [25, 26], $Cp^{*Ph}H$ [27], and AlCp* [2, 3] were prepared according to recent literature methods. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. Melting or decomposition points were determined thermogravimetrically on a Seiko EXSTAR 6300S11 TG/DTA instrument. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^1H, 250.1 MHz; ^{13}C, 62.9 MHz) in C_6D_6 at 298 K unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards.

The crystal structures of **3a**, **4a** and **4b** were measured on an Oxford Excalibur 2 diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.

CCDC-265832 (**3a**), CCDC-265833 (**4a**) and CCDC-265834 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtain free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

$[Cp^{*Ph}AlBr(\mu_2\text{-}Br)]_2$ (1)

A suspension of $K(C_5Me_4Ph)$ (14.0 g, 59.2 mmol) in THF (150 mL) was treated dropwise with Me_3SiCl (6.5 g, 59.8 mmol). The mixture was allowed to stir for 2 h at room temperature. The white precipitate was removed by filtration through Celite and washed twice with THF (2 x 20 mL). The washings and filtrate were combined and the solvent removed *in vacuo* to give $(C_5Me_5Ph)SiMe_3$ as yellow liquid (estimated yield: 11.7 g, 95 %). Subsequently, a suspension of $AlBr_3$ (11.0 g, 41.2 mmol) in hexane (250 mL) was treated slowly (1h) with $(C_5Me_5Ph)SiMe_3$ (12.9 g, 47.7 mmol) at room temperature according to literature. After refluxing the mixture for 3 h, the solvent was removed by means of cannulation. The residue was washed with hexane (2 x 20 mL). Recrystallization in hexane gave the product as white solid. Yield: 9.56 g (60 %).

$AlCp^{*Ph}$ (2)

A Na/K alloy prepared from sodium (0.40 g, 17.4 mmol) and potassium (1.26 g, 32.4 mmol) in toluene (10 mL) was treated with a suspension of $[Cp^{*Ph}AlBr(\mu\text{-}Br)]_2$ (9.56 g, 24.9 mmol) in toluene (30 mL) according to literature. The mixture was allowed to stir for 15 h at room temperature. The resulting gray solid was removed by filtration, and washed with toluene (3 x 20 mL). The solvent was removed *in vacuo* to give a yellow oil. The oil was dissolved in hexane and the solvent again removed *in vacuo*. The residue was recrystallized in diethylether to give a yellow solid. Yield: 4.1 g (73 %). Elemental analysis calcd (%) for $C_{15}H_{17}Al$: C 80.33, H 7.64; found: C 79.83, H 8.86.

^{1}H NMR: (C_6D_6, 250 MHz, 25 °C): δ =7.35 (m, 5 H), 1.92 (s, 6 H), 1.77 (s, 6 H). **^{13}C NMR** (C_6D_6, 62.9 MHz, 25 °C): δ = 136.8 ($C_5Me_4\mathit{Ph}$, 1 C), 131.0 ($C_5Me_4\mathit{Ph}$, 2 C), 130.3 ($C_5Me_4\mathit{Ph}$, 1 C), 126.1 ($C_5Me_4\mathit{Ph}$, 2 C), 121.8 (C_5Me_4Ph, 1 C), 116.1 (C_5Me_4Ph, 2 C), 115.1 (C_5Me_4Ph, 2 C), 12.1 ($C_5\mathit{Me}_4Ph$, 2 C), 11.1 ($C_5\mathit{Me}_4Ph$, 2 C). **^{27}Al NMR** (C_6D_6, 65.2 MHz, 25 °C): $\delta = -102.5$.

$[(dvds)(\mu_2\text{-}AlCp^*)_2]$ (3a)

A mixture of dvds (0.144 g, 0.774 mmol) and $[\{AlCp^*\}_4]$ (0.250 g, 0.387 mmol) in toluene (5 mL) was warmed to 60 °C for 1 h. The

Table 1 Crystallographic data for [(dvds)(μ_2-AlCp*)$_2$] (**3a**) and [M(AlCp*)$_4$] (M = Pd **4a**, M = Ni **4b**)

	[(dvds)(μ_2-AlCp*)$_2$] (3a)	**[Pd(AlCp*)$_4$] (4a)**	**[Ni(AlCp*)$_4$] (4b)**
formula	$C_{28}H_{48}Al_2OSi_2$	$C_{50}H_{75}Al_5Pd$	$C_{40}H_{60}Al_4Ni$
M_T /g mol^{-1}	510.80	755.20	707.51
T /K	103(2)	213(2)	213(2)
crystal system	orthorhombic	tetragonal	tetragonal
space group	*Pbca*	$I\bar{4}$	$I\bar{4}$
a /Å	17.196(10)	12.178(2)	12.1322(19)
b /Å	15.346(8)	12.178(2)	12.1322(19)
c /Å	22.706(9)	15.015(5)	14.867(5)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	90
V /Å^3	5992(5)	2226.6(9)	2188.2(9)
Z	8	2	2
$\rho_{calc.}$ /g cm^{-3}	1.133	1.126	1.074
μ /mm^{-1}	0.195	0.519	0.547
F (000)	2224	796	760
2 θ /°	3.20 − 25.10	2.15 − 25.00	2.74 − 24.99
index ranges	$-19 \leq h \leq 20$, $-18 \leq k \leq 13$, $-27 \leq l \leq 25$	$-14 \leq h \leq 14$, $-7 \leq k \leq 14$, $-17 \leq l \leq 11$	$-14 \leq h \leq 10$, $-14 \leq k \leq 6$, $-17 \leq l \leq 17$
Reflection collected	27732	3002	2809
Reflections unique	5315 [R_{int} = 0.0989]	1921 [R_{int} = 0.0183]	1809 [R_{int} = 0.0250]
goodness-of-fit on F^2	0.958	1.057	1.044
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0603, wR_2 = 0.1245	R_1 = 0.0266, wR_2 = 0.0645	R_1 = 0.0414, wR_2 = 0.0983
R indices (all data)	R_1 = 0.1260, wR_2 = 0.1493	R_1 = 0.0279, wR_2 = 0.0651	R_1 = 0.0442, wR_2 = 0.1015

resulting colorless solution was slowly cooled to −30 °C, whereupon crystals are formed. The colorless crystals were isolated by means of cannulation, washed twice with a small amount of cold hexane and dried in vacuo. Yield: 0.326 g (83 %). m.p. 103 °C (decomp.). Elemental analysis calcd (%) for $C_{28}H_{48}Al_2Si_2O$: C 65.84, H 9.47; found: C 65.57, H 9.32.

^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ = 1.96 (s, 15 H), 1.95 (s, 15 H), 0.55-0.32 (m, 4 H), 0.29 (s, 6 H), 0.11 (s, 6 H), −0.26 (t, *J*(H-H) = 8.7 Hz, 2 H). **^{13}C NMR** (C_6D_6, 62.9 MHz, 25 °C): δ = 114.3 ($\mathit{C}_5\mathrm{Me}_5$), 114.1 ($\mathit{C}_5\mathrm{Me}_5$), 13.8 (CH), 10.7 ($\mathrm{C}_5\mathit{Me}_5$), 10.6 ($\mathrm{C}_5\mathit{Me}_5$), 10.1 ($CH_2$), 3.6 ($SiMe_2$), −0.2 ($SiMe_2$).

[(dvds)(μ_2-AlCp^{Ph})$_2$]* (3b)

A solution of $\mathrm{Cp^{*Ph}Al}$ (200 mg, 0,892 mmol) in toluene (5 mL) was treated with dvds (84 mg, 0,450 mmol). After warming the yellow solution for 1h a colorless solution was obtained. The solvent was removed *in vacuo*. The residue was dissolved in hexane and the solvent again removed *in vacuo* to give a white oil. Yield: 110 mg (60 %).

^{1}H NMR: (C_6D_6, 250 MHz, 25 °C): δ = −0.13 (t, 2 H), 0.13 (s, 6 H), 0.25 (s, 6 H), 0.59 (d, 4 H), 1.99 (s, 6 H), 2.01 (s, 6 H), 2.03 (s, 6 H), 2.08 (s, 6 H), 7.35 (m, 10 H). **^{13}C NMR** (C_6D_6, 62.9 MHz, 25 °C): δ = 136.2 ($\mathrm{C_5Me_4}\mathit{Ph}$, 1 C), 135.9 ($\mathrm{C_5Me_4}\mathit{Ph}$, 1 C), 131.0 ($\mathrm{C_5Me_4}\mathit{Ph}$, 2 C), 130.8 ($\mathrm{C_5Me_4}\mathit{Ph}$, 2 C), 128.9 ($\mathrm{C_5Me_4}\mathit{Ph}$, 2 C), 128.8 ($\mathrm{C_5Me_4}\mathit{Ph}$, 1 C), 128.5 ($\mathrm{C_5Me_4}\mathit{Ph}$, 1 C), 126.5 ($\mathrm{C_5Me_4}\mathit{Ph}$, 2 C), 121.6 ($\mathit{C}_5\mathrm{Me_4Ph}$, 1 C), 120.3 ($\mathit{C}_5\mathrm{Me_4Ph}$, 1 C), 117.5 ($\mathit{C}_5\mathrm{Me_4Ph}$, 2 C), 117.3 ($\mathit{C}_5\mathrm{Me_4Ph}$, 2 C), 114.7 ($\mathit{C}_5\mathrm{Me_4Ph}$, 2 C), 114.6 ($\mathit{C}_5\mathrm{Me_4Ph}$, 2 C), 15.0 (CH), 13.8 (CH), 12.8 (CH_2), 12.1 ($\mathrm{C}_5\mathit{Me}_4\mathrm{Ph}$, 2 C), 11.0 ($\mathrm{C}_5\mathit{Me}_4\mathrm{Ph}$, 1 C), 10.9 ($\mathrm{C}_5\mathit{Me}_4\mathrm{Ph}$, 1 C), 10.8 ($CH_2$), 3.9 ($SiMe_2$), −0.1 ($SiMe_2$).

[Pd(AlCp)$_4$]* (4a):

A suspension of [(tmeda)$PdCl_2$] (0.150 g, 0.511 mmol) and [{AlCp*}$_4$] (0.412 g, 0.639 mmol) in hexane (10 mL) was refluxed for 5 h, whereupon an orange solution and a beige precipitate (Cl_2AlCp*) is formed. After filtration, all volatiles were removed in vacuo. The resulting yellow precipitate was dissolved in hexane and the product was crystallized by slow cooling to −30 °C. Yield: 0.312 g (81 %). m.p. 123 °C (decomp.). Elemental analysis calcd (%) for $C_{40}H_{60}AlPd$: C 63.62, H 8.01; found: C 64.01, H 8.32.

^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ = 1.92(s, 60 H). **^{13}C NMR** (C_6D_6, 62.9 MHz, 25 °C): δ = 113.0 ($\mathit{C}_5\mathrm{Me}_5$), 10.8($\mathrm{C}_5\mathit{Me}_5$). **^{27}Al NMR** ($C_6D_6$, 65.2 MHz, 25 °C): δ = −67.2.

[Ni(AlCp)$_4$]* (4b):

A suspension of [Ni(cod)$_2$] (0.100 g, 0.364 mmol) and [{AlCp*}$_4$] (0.234 g, 0.364 mmol) in hexane (8 mL) was refluxed for 3 h, whereupon an orange solution is formed. After filtration, the yellow solution was cooled to −30 °C, giving the product as a yellow crystalline solid. Yield: 0.312 g (81 %). m.p. 94 °C (decomp.). Elemental analysis calcd (%) for $C_{40}H_{60}AlNi$: C 67.92, H 8.49; found: C 67.67, H 8.54.

^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ = 1.92(s, 60 H). **^{13}C NMR** (C_6D_6, 62.9 MHz, 25 °C): δ = 112.9 ($\mathit{C}_5\mathrm{Me}_5$), 10.7($\mathrm{C}_5\mathit{Me}_5$). **^{27}Al NMR** ($C_6D_6$, 65.2 MHz, 25 °C): δ = −37.7.

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